

Uptake kinetics of 3-buten-1-ol, 4-penten-1-ol and 3-methyl-3-buten-1-ol into sulfuric acid solutions

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Received June 17, 2010; accepted September 7, 2010

Unsaturated alcohols are important components in complex mixtures of oxygenated volatile organic compounds, and play a significant role in atmospheric chemistry. The uptake kinetics of 3-buten-1-ol (BO31), 4-penten-1-ol (PO41) and 3-methyl-3-buten-1-ol (MBO331) into 20 wt%–80 wt% H₂SO₄ solutions were studied, using a rotated wetted-wall reactor coupled to a differentially pumped single-photon ionization time of flight mass spectrometer (SPI-TOFMS). With increasing acidity, the uptake processes changed from reversible to irreversible (reactive). Reactive uptake was observed in 60 wt%–80 wt%, 50 wt%–80 wt% and 30 wt%–80 wt% H₂SO₄ solutions for BO31, PO41 and MBO331, respectively. Reactive uptake coefficients were acquired and are reported here for the first time. Reactivity order followed the trend: BO31 < PO41 < MBO331. An electrophilic addition mechanism of H₂SO₄ to the C=C double bond was used to explain this trend. Atmospheric implications were discussed, based on the reactive uptake coefficients. This heterogeneous reaction with sulfuric acid aerosols may be a potential degradation pathway of unsaturated alcohols, and should not be neglected.

heterogeneous reaction, unsaturated alcohols, reactive uptake coefficients, sulfuric acid, OVOCs

Citation: Xu Z F, Liu Z, Ge M F, et al. Uptake kinetics of 3-buten-1-ol, 4-penten-1-ol and 3-methyl-3-buten-1-ol into sulfuric acid solutions. Chinese Sci Bull, 2011, 56: 1352–1356, doi: 10.1007/s11434-011-4461-8

The scientific community has recently given increasing attention to oxygenated volatile organic compounds (OVOCs), because such species are thought to be important in atmospheric chemistry. Studies have also shown that interactions between OVOCs and acidic particles may have relevance in the formation of secondary organic aerosols [1–4]. Examples of OVOCs are some unsaturated alcohols, which are emitted as primary pollutants from various biogenic and anthropogenic sources. Goldan et al. [5] found that the concentration of 2-methyl-3-buten-2-ol (MBO232) could reach levels of several ppb at a remote Colorado mountain site, exceeding levels of isoprene by a factor of between five and eight. The emission of 3-methyl-2-buten-1-ol (MBO321) and 3-methyl-3-buten-1-ol (MBO331) has

been observed from different vegetation types [6]. Pentenols emitted during leaf drying, senescence, and following freeze-thaw damage were detected by Fall et al. [7]. Other alcohols including 2-buten-1-ol (BO21), 2-methyl-2-propen-1-ol (MPO221) and 3-buten-1-ol (BO31) are also released into the atmosphere during polymer synthesis processes in plastic industries.

These unsaturated alcohols can be removed by reaction with hydroxyl (OH) radicals, ozone (O₃), nitrate (NO₃) radicals, and sometimes also chlorine (Cl), once they enter the atmosphere [8–11]. Compared to researches of these homogeneous reactions, the amount of studies on heterogeneous processes was less, particularly regarding kinetic factors that are necessary for assessing their atmospheric impact. Because of lower volatility than corresponding alkenes, unsaturated alcohols can more readily partition into

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atmospheric aerosols. Nozière et al. [12] performed uptake experiments of MBO232 into sulfuric acid (H_2SO_4) solutions, and found significant reaction potential in 40 wt%–80 wt% H_2SO_4 range. Thus, heterogeneous processes may potentially be an effective degradation pathway.

In the current study, the uptake kinetics of the unsaturated alcohols, BO31, 4-penten-1-ol (PO41) and MBO331, into 20 wt%–80 wt% H_2SO_4 were investigated, and reactive uptake coefficients (γ) were determined. To the best of our knowledge, this study provides the first uptake kinetics measurements for these unsaturated alcohols into H_2SO_4 solution. The potential implications of our findings for the global atmosphere are also discussed.

1 Experimental

Uptake experiments were carried out using a rotated wetted-wall reactor (RWW) coupled to a differentially pumped single-photon ionization time of flight mass spectrometer (SPI-TOFMS), which has been used in our previous studies [13,14]. The RWW consisted of a horizontal glass cylindrical flow reactor equipped with an external glass jacket for thermostat purposes, and a rotating inner cylinder (length $L=30$ cm and inner radius $R=1.25$ cm) for supporting the liquid film. A small volume of H_2SO_4 (3–3.5 mL, corresponding to a film thickness of ~ 0.1 mm) was placed in the inner cylinder, which was rotated at 10–15 r/min to maintain a uniform film on the wall. A glass stirring bar rested on the bottom of the inner cylinder to ensure the solution was sufficiently mixed and could be easily spread. A helium/water vapor mixture in equilibrium with the acidic solution was used as the carrier gas, with a total flow rate of $212 \text{ STP cm}^3 \text{ min}^{-1}$ (STP conditions: 273 K, 1 atm (1 atm = 1.013×10^5 Pa)). This ensured constant solution acidity throughout experiments. Organic reactant compounds were introduced into the main flow of the reactor, by entraining their vapor into helium flow ($21.2 \text{ STP cm}^3 \text{ min}^{-1}$), and allowing this flow through a movable injector centered in the rotating cylinder. The movable injector allowed for contact distance variations between the reactant gas and solution. Gas flows were monitored with calibrated electronic mass flow meters (SevenStar D08-1D/ZM, Beijing, China). All measurements were performed at a total pressure of 5–150 Torr (1 Torr = 1.33×10^2 Pa) and temperature of 293 K.

A differentially pumped SPI-TOFMS was employed to monitor reactant concentration variations in the gas-phase upon uptake. Mass spectra of the three unsaturated alcohols are shown in Figure 1, and all peaks were monitored in case of missing product ions. No ion peak belonging to a product was observed during the uptake measurements. Variation of ion peaks marked by * were used to calculate the uptake coefficients, because of their enhanced signal intensity (molecular ion peak for MBO331 and BO31, and fragment ion

peak for PO41).

BO31 (99%, Alfa Aesar), PO41 (98%, Alfa Aesar), MBO331 (97%, Alfa Aesar), and H_2SO_4 (>96 wt%, Beijing Chemical Reagents Company) were used without further purification. H_2SO_4 solutions were prepared by mixing H_2SO_4 with 18 M Ω -cm deionized water. H_2SO_4 solution composition was determined before and after each experiment by titration with a known concentration NaOH solution, and was found to vary by <0.5 wt%. The H_2SO_4 solution was replaced after each experiment.

2 Results and discussion

2.1 Uptake measurements

Uptake measurements were performed by exposing H_2SO_4 solutions to unsaturated alcohols, while monitoring the unsaturated alcohol signal intensity using VUV-SPI-TOFMS. Adsorption/desorption to/from solutions was evident from the signal decline and recovery. Figure 2 shows the temporal profiles of MBO331 signal during experiments with: (a) 20 wt%, (b) 30 wt% and (c) 60 wt% H_2SO_4 solutions. For these experiments, the injector was moved upstream, thus exposing the H_2SO_4 solutions to MBO331. For the 20 wt% H_2SO_4 solution, the transient signal decreased and then returned to its original level as the H_2SO_4 solution was saturated.

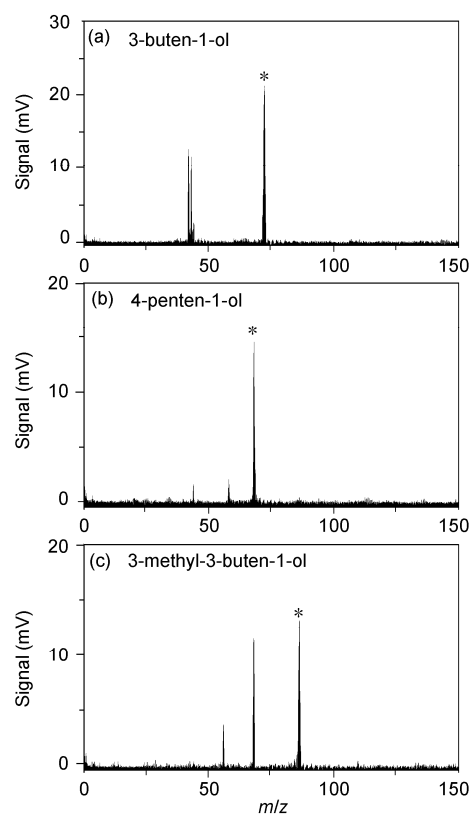


Figure 1 The SPI-TOFMS mass spectra of unsaturated alcohols. Ion peaks marked by * were used to calculate uptake coefficients.

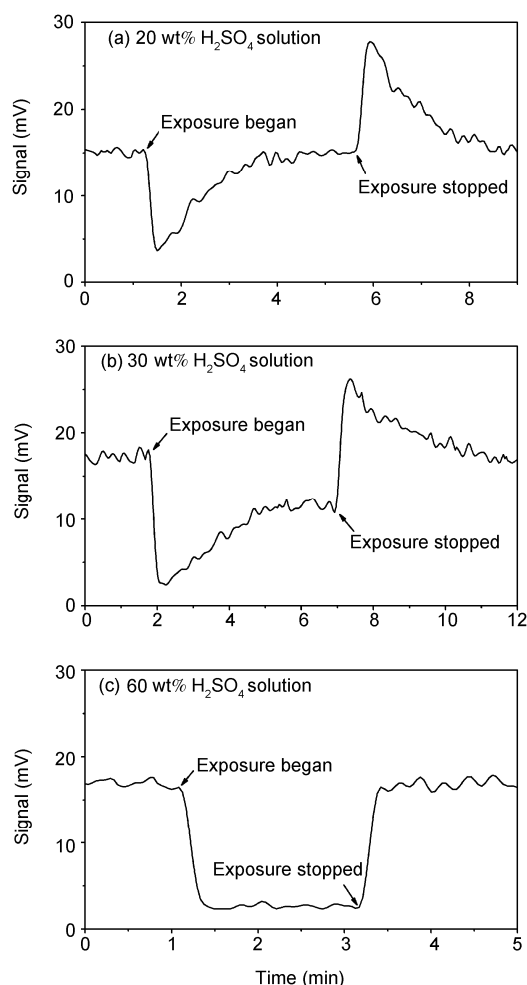


Figure 2 Typical time profiles of the MBO331 signal, showing uptake into (a) 20 wt%, (b) 30 wt% and (c) 60 wt% H_2SO_4 solutions. Observed uptake was (a) reversible, (b) reversible and reactive, and (c) reactive. $m/z=86$

Pushing the injector back to its initial position produced a secondary transient signal, corresponding to the release of MBO331 back to the gas phase. The similarity in shape and total area of the adsorption and desorption curves meant that MBO331 partitioned reversibly between the gas and solution phases. For the 60 wt% H_2SO_4 solution, the uptake displayed a steady-state feature and exhibited no saturation over the experimental time scale, indicating that an irreversible reaction was dominant. In numerous experiments, two behavior types were observed for the variation in MBO331 signal (Figure 2(b)): MBO331 was adsorbed and then subsequently desorbed, but additionally a constant signal offset was observed at a long exposure time. This may have been because of the occurrence of an irreversible reaction.

The plots in Figure 2 suggested that multiple equilibrium/reaction mechanisms existed. At low acidity conditions (20 wt%), dissolution equilibrium played a dominant role, and led to rapid saturation of the H_2SO_4 solution. When the H_2SO_4 solution was no longer exposed, the

MBO331 equilibrium shifted from the liquid to gas phases, corresponding to desorption. As acidity increased, dissolution equilibrium was not the only process occurring within the gas-liquid interaction. Some dissolved MBO331 may have irreversibly been converted to reaction product, resulting in a constant negative signal offset. When acidity increased further (60 wt%), the irreversible reaction became predominant. Only irreversible reaction was apparent in Figure 2(c).

The other two unsaturated alcohols were less reactive to H_2SO_4 than MBO331. BO31 uptake was dominated by a reversible component for 20 wt%–50 wt% H_2SO_4 , and indicated no desorption for 80 wt% H_2SO_4 . Partially reactive uptake of PO41 was observed when solution acidity increased up to 50 wt%, and reversible behavior was not observed for 70 wt%–80 wt% H_2SO_4 . This may have been because of discrepancies in molecular structure of the unsaturated alcohols, which are discussed in detail below.

2.2 Calculation of reactive uptake coefficients

To more accurately compare the reactivity of the three unsaturated alcohols, reactive uptake coefficients (γ) were calculated. The calculation method was stated in detail elsewhere, and only a brief description is listed here [13,14]. When the experiment had just commenced, the movable injector was positioned at its maximum allowable downstream location. Once here, the acidic solution was unexposed to the reactant, and the unperturbed reactant gas concentration could be measured as the original signal, S_0 . The injector was then moved upstream to expose the solution to reactant gas. Reactive uptake was indicated by a constant offset between the original and uptake signals (S) with time. The first-order rate constant for reactant removal from the gas phase, k_{obs} (s^{-1}), was calculated from:

$$\ln\left(\frac{S}{S_0}\right) = k_{\text{obs}} L / v_{\text{ave}}, \quad (1)$$

where L (cm) is the contact distance of the gas and solution, and v_{ave} (cm s^{-1}) is the average gas flow velocity. The surface rate constant for reactant gas removal, $k_{\text{gas-surface}}$ (s^{-1}), can be determined by correcting k_{obs} for diffusion according to the Fuller-Schettler-Gidding method [15–18]. Finally, γ defined as the probability of loss per collision with the surface [19], could be calculated from:

$$\gamma = \frac{4k_{\text{gas-surface}}V}{\omega A}, \quad (2)$$

where ω (m s^{-1}) is the mean molecular speed of the reactant gas, V (cm^3) is the volume of the reaction zone, and A (cm^2) is the geometric area of the exposed solution.

Figure 3 describes the loss of MBO331 as a function of injector position. The variation in $\ln[S/S_0]$ was found to decrease linearly with contact distance. All decays followed

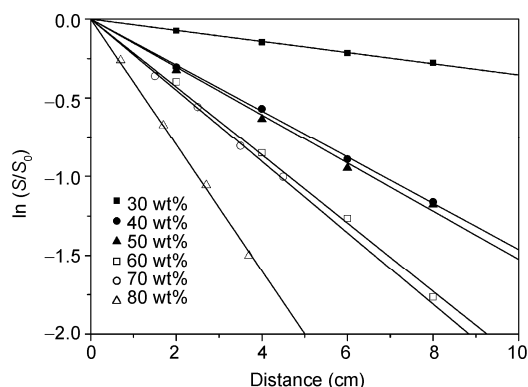


Figure 3 MBO331 signal as a function of injector distance, for 30 wt%–80 wt% H_2SO_4 solutions.

pseudo-first order kinetics, and first-order decay rates (k_{obs}) were obtained from gradients using a linear regression method. After correcting for diffusion, uptake coefficients were determined using eq. (2), and are summarized in Table 1. This process was also carried out for BO31 and PO41.

From the data in Table 1, the reactive uptake coefficient for each unsaturated alcohol showed an increasing trend with acidity, implying that acidity dominated the uptake kinetics. The reactivity of the alcohols followed the trend: $\gamma(\text{BO31}) < \gamma(\text{PO41}) < \gamma(\text{MBO331})$. This could be explained by an electrophilic addition mechanism of H_2SO_4 to the $\text{C}=\text{C}$ double bond. The substituent pattern of carbon atoms in a $\text{C}=\text{C}$ double bond affects the bonds electron distribution. For MBO331 the methyl group connected to the $\text{C}=\text{C}$ double bond exerted a strong positive inducing effect, and rendered the double bond susceptible to electrophilic attack. Thus, MBO331 was more reactive to H_2SO_4 than the other unsaturated alcohols in this study. PO41 has a longer chain substituted group, which led to greater electron-donating ability than for BO31. In addition, the greater distance between the hydroxyl group and double bond in PO41 led to a lesser electron-withdrawing effect. Thus, the $\text{C}=\text{C}$ double bond of PO41 could be attacked more readily than that of

BO31.

The acidity of aerosols and cloud condensation nucleus (CCN) has been reported to be in the range of pH 2–5 [20,21]. However, significantly higher sulfate aerosol acidity, approaching values used in this study has also been reported [22,23] and used in other experiments [24–27]. Thus, this heterogeneous reaction could potentially occur in the ambient atmosphere. To elucidate the atmospheric significance of the uptake of BO31, PO41 and MBO331 into sulfuric acid aerosols, their loss rates at typical atmospheric conditions need to be determined. Experimental data from this study allows the individual estimation of atmospheric lifetimes for these three unsaturated alcohols, for their reaction with H_2SO_4 . After consulting atmospheric conditions of H_2SO_4 content [22,23], γ values were adopted from 60 wt%–80 wt% H_2SO_4 data given in Table 1. The atmospheric lifetimes, τ , of the unsaturated alcohols with regard to their uptake into H_2SO_4 solution could be estimated by: $\tau = 4/\gamma\omega\sigma$, where ω is the mean molecular speed of the alcohol, and σ is the area density of the atmospheric sulfate aerosol ($\sim 2 \times 10^{-7} \text{ cm}^2/\text{cm}^3$ [28]). This calculation provided atmospheric lifetimes of 74.9–1.1 d for BO31, 17.4 d to 10.1 h for PO41 and 4.0 d to 8.0 h for MBO331. Compared to homogeneous reactions with $\text{OH}/\text{O}_3/\text{NO}_3$, which lead to atmosphere lifetimes of a few hours [8,10], the heterogeneous reaction is expected to be less important. However, irreversible reactions resulted in atmospheric lifetimes of a few hours for PO41 and MBO331, when the solution acidity increased to 80 wt%. Such lifetimes are very close to the homogeneous reaction values mention above. Thus, the heterogeneous reaction with sulfuric acid aerosols may be a significant degradation pathway for unsaturated alcohols. This is particularly so for freshly nucleated aerosols potentially formed prior to any neutralization.

3 Conclusions

Unsaturated alcohols are important components in complex

Table 1 Reactive uptake coefficients with varying wt% H_2SO_4 solutions

H_2SO_4 (wt%)	$\gamma^a (\times 10^{-4})$		
	BO31 <chem>CH2=C(H)CH2CH2OH</chem>	PO41 <chem>CH2=C(H)CH2CH2CH2OH</chem>	MBO331 <chem>CH2=C(CH3)CH2CH2OH</chem>
20	—	—	—
30	—	—	0.33±0.02
40	—	—	3.27±0.11
50	—	0.73±0.03	15.98±1.12
60	1.05±0.05	4.95±0.35	21.31±1.04
70	5.56±0.11	22.15±0.91	63.56±2.20
80	68.57±2.63	205.27±10.70	256.48±10.43

a) Each value is the average of at least three measurements, and the error corresponds to one standard deviation (σ).

mixtures of OVOCs, which are emitted from biogenic and anthropogenic sources, and are relevant in atmospheric chemistry. The present study addressed the uptake kinetics of BO31, PO41 and MBO331 into H_2SO_4 solutions with composition ranges of 20 wt%–80 wt%. Reactive uptake coefficients were acquired and reported for the first time (60 wt%–80 wt%, 50 wt%–80 wt% and 30 wt%–80 wt% for BO31, PO41 and MBO331, respectively), indicating that H_2SO_4 acidity controlled the reactive uptake kinetics. Reactivity followed the trend $\text{BO31} < \text{PO41} < \text{MBO331}$, which may have been because of the electrophilic addition mechanism of H_2SO_4 to the $\text{C}=\text{C}$ double bond. Atmospheric lifetimes of the three unsaturated alcohols were estimated. These suggested that heterogeneous reaction with sulfuric acid aerosols may be a potential degradation pathway, and should not be neglected.

This work was supported by the Knowledge Innovation Program of Chinese Academy of Sciences (KJCX2-YW-N24, KZCX2-YW-205) and the National Natural Science Foundation of China (40925016, 40830101).

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